

CHARACTERIZATION OF SURFACE ENERGY EFFECTS ON MORPHOLOGY OF THIN DIBLOCK COPOLYMER FILMS BY HIGH THROUGHPUT TECHNIQUES

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Introduction

Block copolymers are widely used materials due to their unique capabilities as surfactants, adhesives and ordered templates. An understanding of the properties of these materials is crucial for their increased use as polymer materials. When symmetric diblock copolymer are cast as thin films, preferential interfacial interactions induce ordering with the formation of lamella parallel to the substrate.¹⁻³ The surface of the film remains smooth when the film thickness, h , is integral multiples of the bulk lamella spacing, L_o , and surface island and hole patterns form when the film deviates from these characteristic thicknesses.⁴⁻⁶ We have recently extended the study of these materials by applying high throughput, continuous gradient techniques to understand the entire morphological evolution of this surface pattern as a function of h .⁷⁻⁹ It has also recently been observed that changes in the morphology of the block copolymer film can be induced by modifying the substrate surface energy.¹⁰⁻¹² The objective of the present work is to combine the thickness gradient technique previously utilized with a surface energy gradient to map out the effect of surface energy on the thin film block copolymer morphology.

Previous studies have shown that when PS-*b*-PMMA is cast and annealed on a hydrophilic substrate the PMMA preferentially segregates to the substrate while the PS segregates to a hydrophobic substrate.^{1,2} The PS block segregates to the air interface in all cases and smooth films form for film thicknesses of $h_s = mL_o$ for the hydrophobic substrate and $h_s = (m + \frac{1}{2})L_o$ for the hydrophilic substrate. Islands and holes are produced when the film thickness deviates from h_s . In films where the substrate is energetically neutral, the block copolymer lamellae are found to form perpendicular to the substrate with a layer of PS across the air interface, producing a smooth film for any h . The objective of this research is to utilize continuous gradient techniques to systematically quantify film surface morphological transitions with changing substrate surface energy.

Experimental

Near symmetric polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) diblock copolymer with $M_n = 51$ kg/mol and $M_w/M_n = 1.05$ were purchased from Polymer Source Inc. and used as received.^{13,14} Gradients were prepared on Si wafers (10 cm, Polishing Corporation of America) that were "piranha etched" to form a native SiO_x surface layer. After cleaning, the wafer is placed in an octyltrichlorosilane solution to form a self assembled monolayer (SAM) on the surface.¹⁵ This SAM is then exposed to UV radiation through a fused silica linear variable density filter that induces a systematic variation in surface chemical functionality with dosage across the sample and a commensurate gradient in surface energy. The change in surface functionality is quantified by TOF-SIMS (not shown here) that indicates a gradient in the density of terminal -COOH moieties across the substrate. The substrate surface energy is characterized by measuring the water contact angle, ϕ , as shown in Fig. 1.¹⁶ Here three images (Fig. 1a-c) of droplets from various locations on the substrate are shown with a plot of the contact angle vs. position for the entire gradient. The plot shows that the contact angle varies linearly across the gradient length. Once the surface energy gradient is formed, a thin film of the block copolymer with a thickness gradient is placed orthogonal to the surface energy gradient using the flow coating method described previously.^{8,17} Film thickness is characterized using an automated 0.5 mm diameter UV-visible interferometry (with standard uncertainty ± 1 nm at 500 nm film thickness) every 2 mm across the gradient sample. After determination of the film thickness the sample is annealed at 170 °C under vacuum to allow ordering of the film. The surface patterns formed are then studied utilizing atomic force microscopy (AFM, Digital Nanoscope Dimension 3100) to determine the effect of surface energy on the block copolymer morphology.

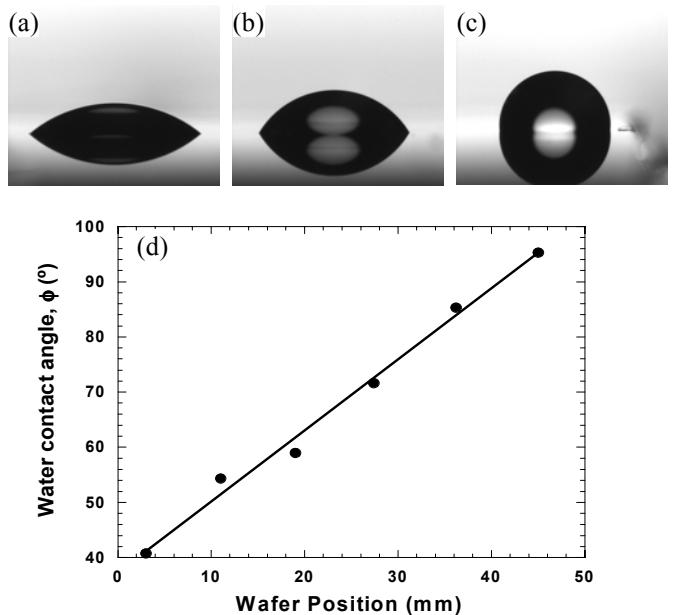


Figure 1. Optical images of water droplets on the substrate at position (a) 3 mm, (b) 19 mm and (c) 45 mm demonstrating the change in contact angle with position. The plot (d) shows the nearly linear change in substrate water contact angle, ϕ .

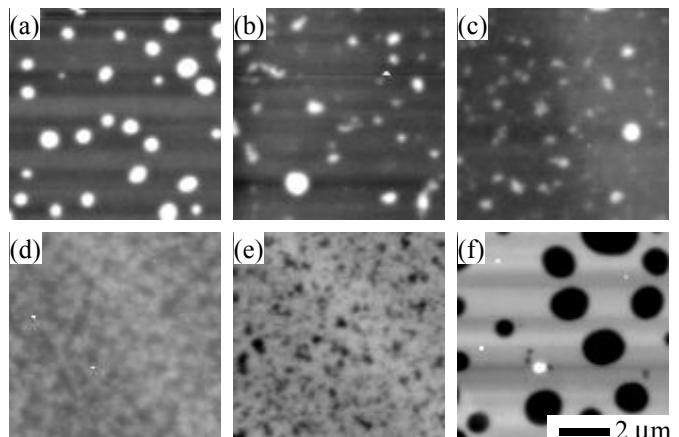


Figure 2. AFM micrographs of the surface morphology of a film annealed 15 h with $h \approx 70$ nm at contact angles of (a) 86°, (b) 83°, (c) 81°, (d) 76°, (e) 73° and (f) 71°.¹⁶ The morphology evolves from islands to holes with decreasing ϕ . Higher topography corresponds to lighter colors.

Results and Discussion

Figs. 2, 3 and 4 show a series of AFM micrographs demonstrating the representative morphology of the block copolymers films after annealing for 15 h as a function of h and ϕ . In Fig. 2 the film $h \approx 70$ nm and ϕ varies from 86° to 71°. In these micrographs, the initial morphology is seen as islands (Fig. 2a) which decrease in size as the contact angle decreases. For ϕ of 76° and 73° (Fig. 2d,e) the island and hole morphologies appear to vanish with only a small amount of surface roughness found in the micrographs. As ϕ decreases to 71° (Fig. 2f) holes become the dominant morphology. This figure demonstrates the expected effect of the surface energy on the morphology, a transition from one surface pattern feature to another as the substrate preference changes from one block to the other. This morphological transition is also observed in Fig. 3 where $h \approx 75$ nm and the contact angles vary from 86° to 73°. The high angle contact angle region morphology is co-continuous and changes to holes as the contact angle decreases. Likewise, a morphological transition is observed in Fig. 4 where $h \approx 80$ nm and ϕ varies

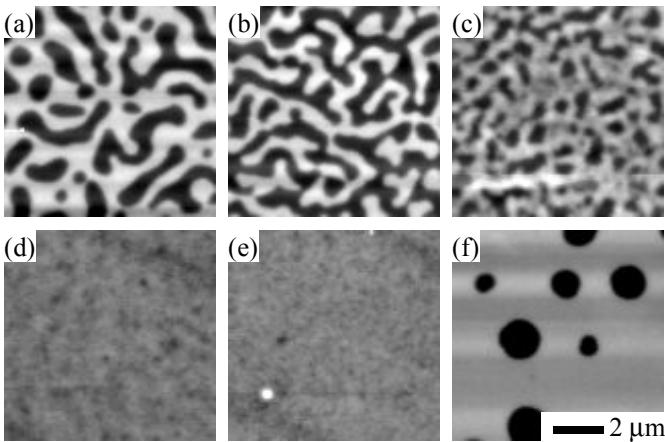


Figure 3. AFM micrographs of the surface morphology of a film annealed 15 h with $h \approx 75$ nm at contact angles of (a) 86°, (b) 83°, (c) 81°, (d) 78, (e) 76° and (f) 73°.¹⁶ The morphology evolves from islands to holes with decreasing ϕ . Higher topography corresponds to lighter colors.

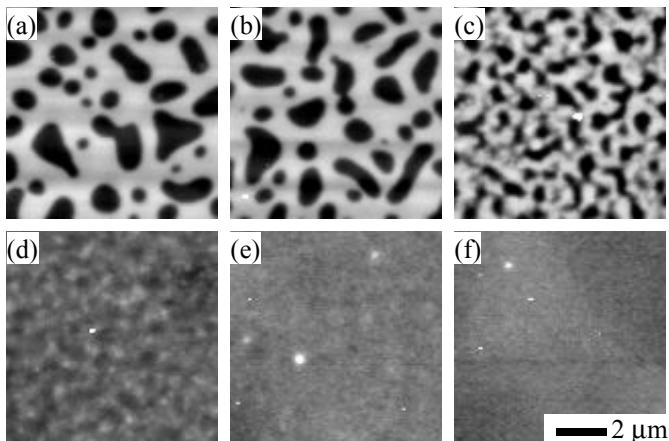


Figure 4. AFM micrographs of the surface morphology of a film annealed 15 h with $h \approx 80$ nm at contact angles of (a) 89°, (b) 86°, (c) 83°, (d) 81, (e) 78° and (f) 76°.¹⁶ The morphology evolves from islands to holes with decreasing ϕ . Higher topography corresponds to lighter colors.

from 89° to 76°. The hole morphology at high ϕ transforms to a smooth surface as ϕ decreases.

One interesting feature of Figs. 2-4 is the gradual loss of morphological definition as ϕ approaches the transition point. This effect produces a decrease in the size of the system morphology, as the preference for one of the blocks becomes weaker. To confirm that this morphological change is thermodynamic in nature and not kinetics, additional annealing of the sample has been performed. The results of this annealing are shown in Fig. 5 where AFM micrographs from a film with $h \approx 75$ nm, annealed for 30 h with ϕ ranging from 86° to 73° are presented. This figure corresponds to Fig. 3 after 15 h additional annealing. While the overall morphology has increased in size, the basic morphologies and their changes are retained, including the transition from one surface pattern to another. The morphology also decreases in size with decreasing ϕ , as found in the 15 h samples, indicating that the decrease in morphological size is due to energetic effects.

Conclusions

The high-throughput measurements presented above validate the effect of substrate surface energy on the structure of block copolymer thin films as shown in previous measurements demonstrating the energetic preference of the substrate switching from one block to another (symmetric to asymmetric ordering). However, the measurements also lead to discovery of novel phenomenology, such as a gradual decrease in the lateral scale of the features as the crossover is approached. By combining a continuous gradient in surface energy orthogonal to a continuous gradient in film thickness, we efficiently

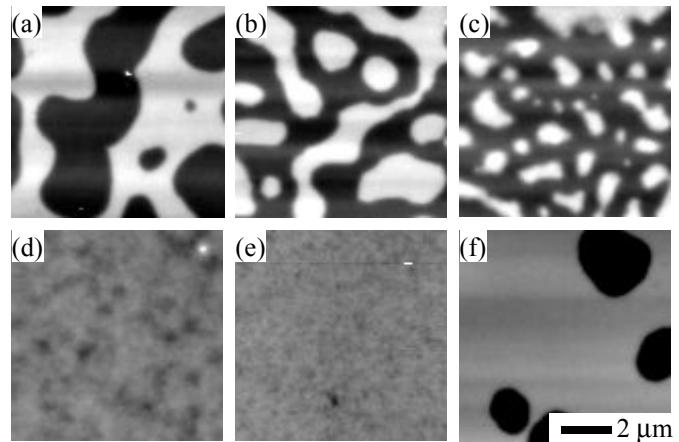


Figure 5. AFM micrographs of the surface morphology of a film annealed 30 h with $h \approx 75$ nm at contact angles of (a) 86°, (b) 83°, (c) 81°, (d) 78, (e) 76° and (f) 73°.¹⁶ The morphology evolves from islands to holes with decreasing ϕ . Higher topography corresponds to lighter colors.

map out the transition from one block copolymer morphology to another as a function of ϕ for multiple film thicknesses. Further work will be aimed at quantifying the substrate surface energy at the crossover point, ascertaining effects of kinetics with extended annealing and more detailed observations of morphology within the block copolymer thin film.

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- Certain equipment, instruments and materials are identified in the paper to adequately specify the experimental details. Such identification does not imply recommendation by NIST.
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